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14. ABSTRACT

This report results from a contract tasking Tel Aviv University as follows: We suggest a methodology to construct a new hybrid vertical device, suitable for electrical activation and operation of organic molecules. Using a vertical architecture, based on silicon technology, it is possible to construct an area of 'standing' molecules, completely encapsulated between two metal electrodes. The fabrication process flow consists of a patterned gold layer, as a bottom electrode, Si3N4 layer as a dielectric platform, nano-cavities (50nm x 50nm) etched into the Si3N4 layer at the center of the electrode. Subsequently, molecules are self-assembled onto the bottom surface of the nano-cavities. The next step is a selective deposition of gold nanoparticles on the top-side of the molecular layer, acting as the metallic contact. The final step is a delicate deposition and patterning of a palladium top electrode. Using this method we suggest a construction of multi-layer arrangement which could form a molecular-circuit. Recently we have demonstrated the construction and operation of single devices array. An array of several thousands of these devices per single silicon wafer are now routinely prepared in our lab in 50% yield (compared to 5-10% yields afforded by other methods). Current Vs voltage (I/V) measurements of these devices indicate that these devices can be charged and thus can be used for electronic storing applications. In the next stage of the process we will focus on construction of ultra-dense molecular circuits using our proposed vertical architecture.

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Final Scientific report
Towards Molecular-Based circuits

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Three dimensional nanometric vertical circuits have been theoretically proposed by Stan. Such circuit, termed "Goto pair" (Fig. 1), can be used to latch digital data and provide signal restoration using only two-terminal devices. This circuit consists of two Negative Differential Resistance devices in series leading to three operating points, two stable and one unstable.

If multiple lines drive its inputs, a Goto pair can be used as a building block for a majority logic gate, the output of which simply takes on the value of the majority of its inputs.

In the first part of this research we have concentrated on development of solid-state template which can serve as a platform for GOTO pair. Our suggested configuration consisted of multiples arrays comprised of various types of self assembled monolayers (SAMs) arranged in vertical configuration (Fig 2) . Each floor consists of different type of molecular layer, therefore leading to multiple molecular GOTO circuits.

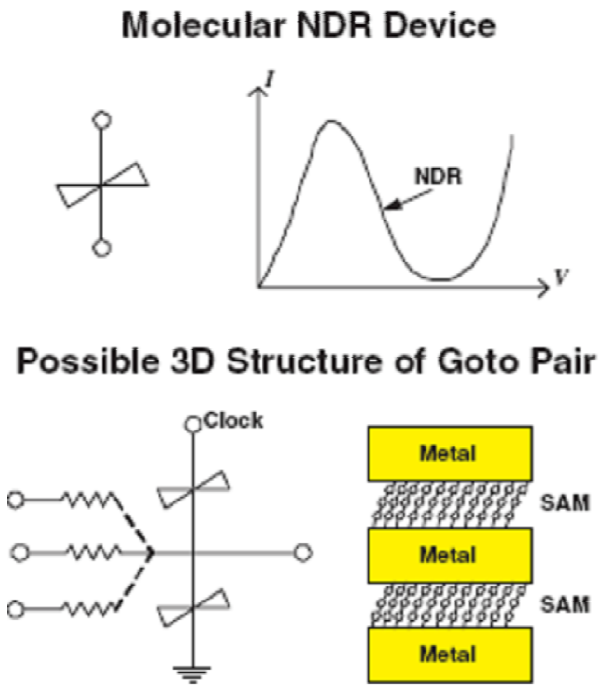

Figure 1 suggested GOTO pair (see ref 1)

As prototype molecules we have chosen modified ferrocene film (Figure 2 compound 1) , and a the protein Azurin (Az). The Fc-based SAM can be used as a candidate for the bottom layer as we have previously shown that SAM1-based film show stable-multi NDR peak properties. SAM2-based films electrical properties are well known and could be served as indication for successful film formation.

The circuit fabrication steps consist of new and novel processes that include successful integration of molecular deposition, and solid-state conventional processes. Special care was taken to prevent possible damage to the molecular and biological films.

Figures 2- 4 shows a representative scheme our first molecular circuit, the process steps and optical images of the circuit respectively.

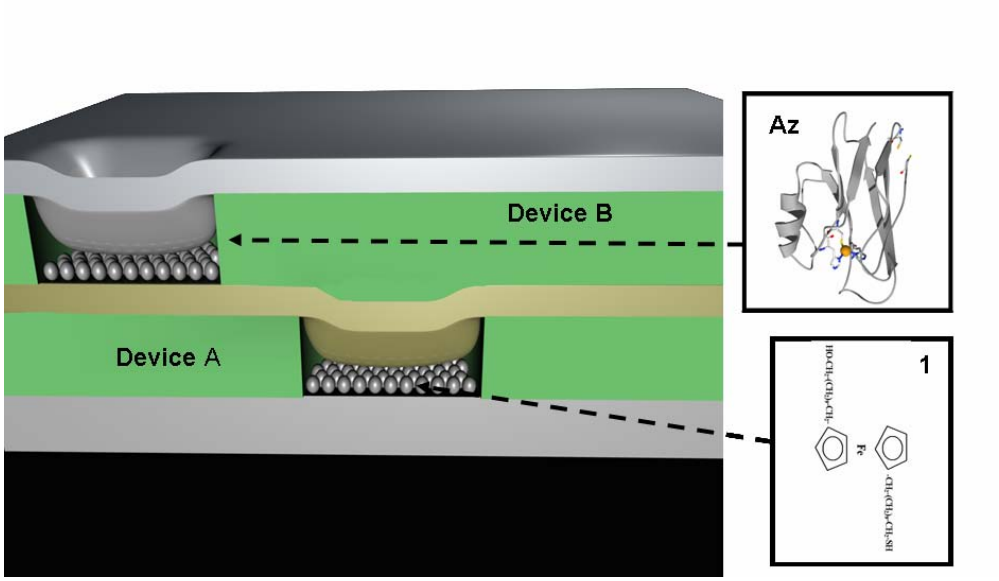

Figure 2 prototype of the molecular circuit. Scheme of the molecular circuit- Two floor-based circuit composed of two different molecular layer was fabricated using our novel methodology. (b). Optical microscope image of the molecular circuits the first (Material: Au), middle (Pd-Au) and top (Pd) electrode are indicated by arrows.

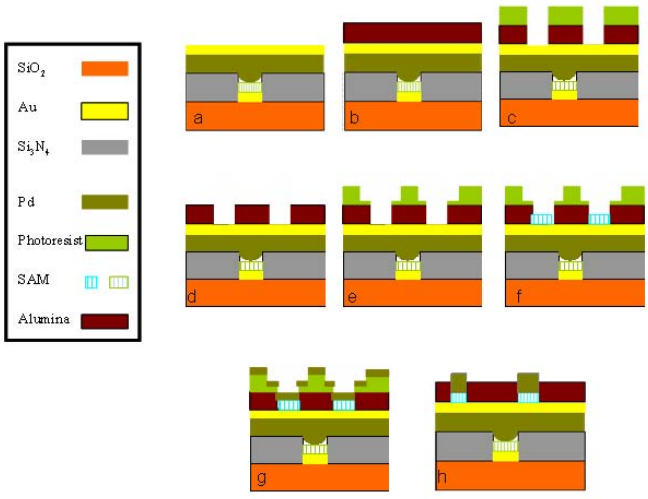

Figure 3 a. The first floor, consisting of compound 1, was constructed with the use of a previously-described recipe,[9] followed by indirect evaporation of a gold layer on top of a

palladium electrode. b. The fabrication process of the second floor was initiated by a cold evaporation of a 100nm alumina layer followed by the definition of microcavities and pads in this layer (c & d). Each second-floor cavity was set between two first-floor junctions with the use of standard etching and lift-off recipes. e. The top electrodes of the second floor were defined with the use of a low-temperature S1818 photolithography–based recipe, followed by the deposition of an Az-based SAM inside the second-floor cavities (f.) . The process was completed by the indirect evaporation and lift-off of the Pd upper contact (g,h)

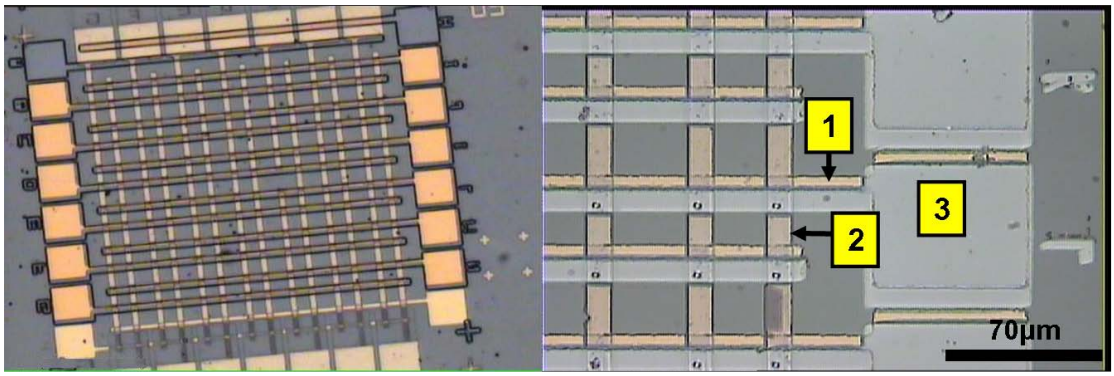

Figure 4 Figure 3 Optical images of the 3D molecular circuit at various stages of the fabrication process. Left. A two-floor 3D molecular circuit after stage f (Figure 3) of the process. Each floor consists of 8x8 single devices. Right. The complete 3D molecular circuit featuring the bottom (1) middle (2) and top (3) terminals.

To evaluate the performance of the circuit, we performed electrical measurements of each floor separately along with leakage current experiments.

The first floor was constructed with compound **1** serving the active component with the use of a previously-published procedure. The same methodology, with minor adjustments to the process flow, was then repeated in order to construct the second floor which was composed of the Az-SAM (see figure 2). Here, Alumina (Al_2O_3) served as a dielectric layer (Figure 3b) instead of the Silicon nitride used for the first-floor construction. Alumina was chosen because it can be evaporated at low power, providing a high-dielectric material which is also transparent. The transparency of this dielectric layer is highly desirable in that it simplifies the alignment of the different floors. These adjustments were needed in order to reduce possible damage to the bottom floor due to the excessive heating that can be generated in conventional photolithography processes. Furthermore, one can not duplicate the first-floor process since it involves some high temperature steps (such as e-beam lithography processes and Plasma Enhanced Chemical Vapor Deposition). Note that the 3D construction process could only be applied because each floor was built on top of a fully-aligned

and encapsulated SAM in the bottom layer. In principal, this process is not limited for two-floors and can be utilized for the construction of unlimited numbers of floors.

Figure 5left shows a room-temperature current vs. voltage (I/V) transport data taken for compound **1** encapsulated in the bottom floor. A clear asymmetrical I/V curve with a distinct imprint of an NDR peak is measured. We and others previously observed this peak. It was attributed either to resonance processes occurring in the metal-SAM-metal junctions or to two-electron process taking place at the Fc moiety (compound **1** figure 2).

We note that the voltage of the NDR peak measured here fits well with previous reports. Several theoretical and experimental studies found redox-center peaks for alkyl-Fc-based molecules near 0.9 volts with voltage shifts attributed to either the length of the alkyl chains or to the nature of the metal contacts. Another explanation for this peak could be the existence of a one-step coherent transport process (resonance mechanism) in which an electron tunnels into the redox center (or other empty molecular levels) and to the other metal electrode without relaxation.

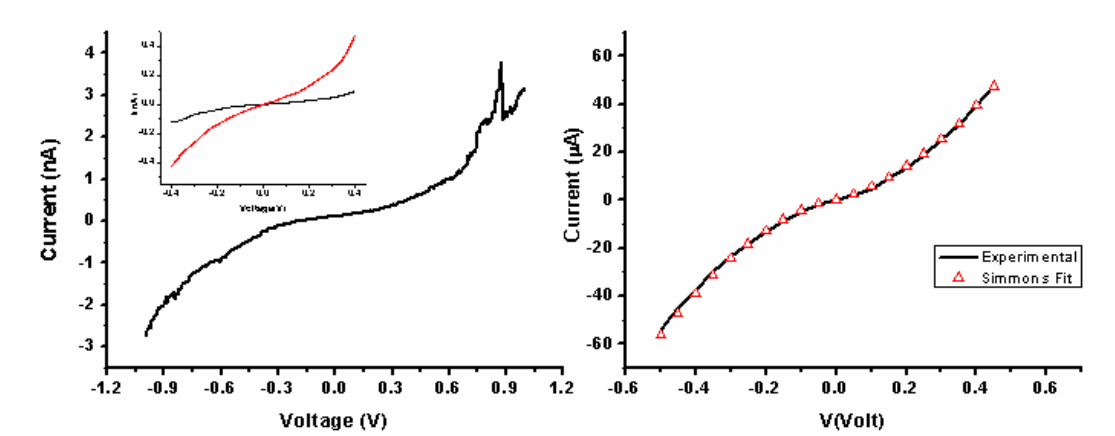

Figure 5. I/V curve taken for the first (left) and second (right) floors. Left I/V taken for compound 1. A typical NDR peak is measured. Inset. I/V curve of compound 1 taken before (black) and after (red) the assembly of the second floor. Right. I/V curve (solid line) and Simmons fit (triangles) taken for the Az-SAM located at the second floor.

However, differences were found between the data obtained for a one-floor device and the current data: first, the aspect ratio of the NDR peak taken in the 3D circuits

was found to be much lower than that of a single-floor device, and second, an additional NDR peak at around 0.5V that is frequently found in Fc-based devices, was not observed here.

Comparison of the two fabrication processes suggest that the thermal treatment performed during the second-floor's fabrication process altered the electrical properties of the 3D device. A clear demonstration of this phenomenon can be seen in Figure 5 left (inset) , which shows the I/V curves around the origin taken for the first floor before (black) and after (red) the construction of the second floor. It is clearly seen that the thermal treatment increased the current measured in the bottom floor. A similar reduction in the performance of devices stacked in the bottom floor of 3D circuits was recently noted by other groups in the case of plastic transistor devices. They attributed this phenomenon to the longer time of exposure and larger number of process steps experienced by the first-floor devices during fabrication of the circuit .

In our case, we attribute this change to a possible Pd top-contact modification resulting from the thermal treatment. We have previously indicated that the top contact in a vertical molecular device is extremely process-sensitive and this can cause considerable change in the location of the NDR peak and its aspect ratio. Since the peak location has not changed and the overall current is on the same order of magnitude, we can eliminate the possibility of filament formation (FF). The latter process would have been expected to show an exponential amplification of the current; this was not observed in our case. Alternatively, a Pd thermal rearrangement without FF can add some additional conduction routes to the molecular junction without causing a dramatic increment in the current . We thus conclude that the Pd-induced thermal damage due to the construction process of the second floor might have reduced the efficiency of the bottom-floor devices.

Figure 5right shows I/V curves of the Az-SAM taken independently in the second floor. In this floor, the cavity diameters were one order of magnitude larger than those in the first floor (1-3 μm and 150nm, respectively). The percentage of working devices decreased dramatically in the large cavities of the second floor (3μm)

compared to the 1μm cavities, probably as a result of the high concentration of pinholes in the Az-based monolayer that resulted in the shortening of the devices.

Surprisingly, the pattern of the Az I/V curves were almost identical to those obtained by CAFM. The observation that the magnitude of the current measured in our device is much larger than that measured in the SPM experiment, implies that total current is the results of the ET through large number of non-interacting Az molecules .

ET analysis of the Az layer was performed with the use of the well-known Simmons-type tunneling model which assumes charge transport between two electrodes separated by a thin insulating layer .

ere we assume that the barrier height, φ , is higher than the applied voltage, *V*; hence a modified Simmons formula for the intermediate voltage range can be applied.. In this model the current density, J, can be estimated as

$$J = \frac{e}{2\pi h(\beta s)^2}\left\{\left(\varphi - \frac{eV}{2}\right)\exp\left[-\frac{4\pi\beta s}{h}(2m)^{0.5}\left(\varphi - \frac{eV}{2}\right)^{0.5}\right] - \left(\varphi + \frac{eV}{2}\right)\exp\left[-\frac{4\pi\beta s}{h}(2m)^{0.5}\left(\varphi + \frac{eV}{2}\right)^{0.5}\right]\right\}$$

where *e* and *m* are the charge and mass of the electron respectively, *s* is the thickness of the protein layer, β is the Simmons factor and *h* is Planck's constant .

The fitting of this model to our data is shown in Figure 5right (triangles). The value of φ for this system can be extrapolated with the use of the fitting data and it is found to be 1.5eV, thus justifying the assumption of an intermediate-range regime. This value is comparable to the 1.05-1.25eV values found in a CAFM experiment[24]. Since we assume that each molecule acts as "an independent dielectric material", the ET per molecule can then be estimated by dividing the overall current by the total number of Az molecules inside the cavity (~ 10^4), giving value of several nA/molecule. This value is consistent with previous findings, indicating that protein SAMs in solid-state devices obey scaling rules and thus can be used as stable materials in large-scale molecular device.

In addition we have evaluated the coupling between the floors. Figure 6 shows I/V data taken between the upper contact of the top floor (electrode 3 Figure 4 right) and the bottom contact of the first floor while the middle electrode is disconnected. Thus, this "leakage current" can be measured only if at least one of the floors is shortening. This can be due to several processes such as pinholes and filament formation. It can be seen that the leakage currents measured are substantially smaller than the currents obtained separately for the first and second floors (at least 4 orders of magnitudes lower than the lowest currents obtained for similar voltages for individual devices). This observation indicates that the floors are not electrically coupled and undesired "cross talking" processes do not take place thus allowing the operation of the vertical circuit.

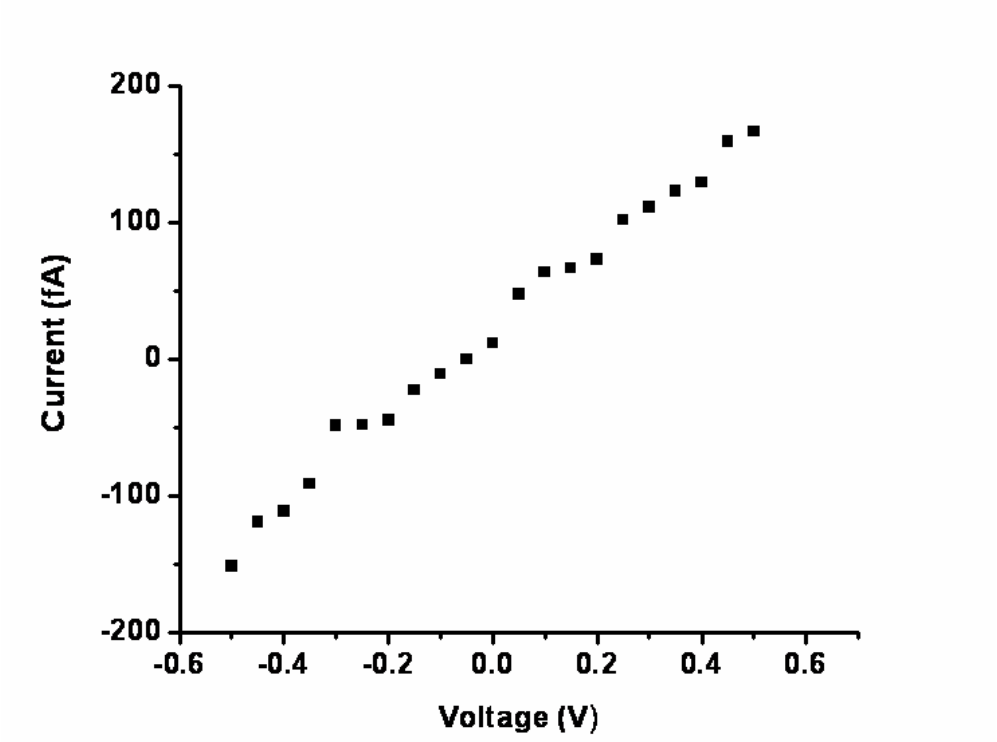

Figure 6 . Leakage current measured (in fA) between the top contact of the second floor and the bottom contact of the first floor. The leakage current at high voltages is at least four orders of magnitude lower than the lowest currents obtained at similar voltages for individual devices.

In conclusion, we have demonstrated a new method for the construction of 3D multifunctional SAM-based vertically stacked molecular junctions. Our approach

involves the sequential formation of encapsulated metal-SAM-metal junctions in a 3D configuration to form a molecular circuit .

The electrical properties of each layer can be manipulated by choosing different compounds for each floor. We have demonstrated this concept by introducing redox-based molecules and proteins into a two-floor circuit and evaluating their electronic properties separately.

In the future, this method should allow the assembly of multilayer multifunctional 3D molecular circuits and lead to a new type of dense and fast circuit.